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OXIDATION AND EMBRITTLEMENT IN SILICIDE-COATED COLUMBIUM-ALLOY  
AND ALUMINIDE-COATED TANTALUM-ALLOY SHEET

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SUMMARY

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Results of a study of silicide-coated Cb-10Ti-5Zr columbium-alloy and aluminide-coated Ta-10W tantalum alloy are presented. Data obtained in static and dynamic oxidation tests, mechanical property tests, and metallurgical examinations of small specimens are discussed.

For the 0.020-inch-thick columbium-alloy sheet with a chromium-titanium-silicon coating, results indicate that, while useful oxidation lifetimes can be provided to at least 2400° F, permeation of embrittling gases through the coating and rapid diffusion throughout the substrate along grain boundaries during cyclic oxidation tests can cause severe embrittlement of the substrate. This can occur prior to coating failure in some instances. A possible mechanism for this embrittlement is postulated.

For the 0.008-inch-thick tantalum-alloy sheet with an aluminum-tin-molybdenum coating, results indicate that useful oxidation lifetimes and substrate ductility could be retained in static oxidation tests to 2900° F at atmospheric pressure but that coating evaporation could limit its usefulness in low-pressure environments. Dynamic oxidation conditions lowered coating lifetimes considerably. Preliminary results with a new coating of higher molybdenum content indicate longer lifetimes in dynamic oxidation tests. Loss of substrate thickness due to solid-state diffusion during high-temperature



exposures is shown to be of considerable magnitude and might be a limiting factor in some applications.

## INTRODUCTION

Several refractory metal studies at the Langley Research Center of the National Aeronautics and Space Administration are directed at the use of columbium and tantalum alloys in the external heat shields of thermal protection systems for aerospace vehicle structures. For applications such as this, these refractory metals must be utilized in thin gages and coated to prevent catastrophic oxidation. Embrittlement of the refractory metal substrate by the coating application or subsequent high-temperature exposure can be a limiting factor in the use of these heat shields. Previous Langley studies on coated molybdenum-alloy sheet and results of tests on coated molybdenum-alloy heat-shield panels are reported in references 1, 2, and 3. Preliminary studies on coated tantalum-alloy panels are reported in reference 4.

Studies of various coatings for columbium alloys have indicated that modified silicide pack cementation coatings containing chromium and titanium are among the most promising of the available coatings. (See, for example, refs. 5 and 6.) One of the first coatings to show promise for providing usable oxidation protection for tantalum alloys was the slurry-dip 23.5 percent (by weight) aluminum-71 percent tin-5.5 percent molybdenum coating (ref. 6). Of the columbium and tantalum alloys available when these studies began, the Cb-10Ti-5Zr alloy and the Ta-10W alloy were selected as having adequate mechanical properties, being compatible with the above-mentioned coatings, and being available in gages and sheet widths and quantities required for heat-shield fabrication.

This paper presents results of oxidation, mechanical property, and metallurgical tests on small specimens. Data of this type must be available before meaningful design, fabrication, and testing of full-size heat-shield panels can be attempted. Static oxidation test results for atmospheric and reduced pressures and dynamic oxidation test results are presented. Temperatures from 2000° F to 3000° F were investigated. Results of room-temperature tensile and bend tests are included along with results of metallurgical examinations for specimens as coated and after various exposures. These examinations were particularly aimed at investigations of embrittlement phenomena.

#### SPECIMENS AND COATINGS

The specimens used in this study were small oxidation coupons  $3/4$  inch by  $1\frac{1}{2}$  inches, tensile strips  $4\frac{1}{8}$  inches by  $5/8$  inch with a 2-inch reduced section  $3/8$  inch wide, and leading-edge segments of  $1/2$ -inch radius by  $1\frac{1}{2}$  inches wide. These specimens were fabricated from columbium-10 percent titanium-5 percent zirconium (by weight) alloy sheet, 0.020-inch-thick (nominal) and tantalum-10 percent tungsten alloy sheet, 0.008 inch thick.

The columbium-alloy sheet specimens were coated with a columbium silicide pack cementation coating modified with chromium and titanium. The tantalum-alloy specimens were coated with a slurry-dip 23.5 percent aluminum-71 percent tin-5.5 percent molybdenum coating in cooperation with the U.S. Air Force. This coating will be referred to as an aluminide coating. A few leading-edge segments were coated with a modified aluminide coating, containing 7 percent molybdenum.

## TEST PROCEDURES

Static oxidation tests were conducted in vertical tube furnaces. The columbium-alloy coupons were supported in zirconium silicate boats and the tantalum-alloy coupons were supported in high-purity alumina boats. Specimens were continuously weighed during the continuous oxidation tests; a 5-percent change in specimen weight was used as a coating failure criterion. During the cyclic tests specimens were rapidly inserted into the furnaces, reaching 95 percent of test temperature within 30 seconds, exposed at temperature for 1 hour or 6 minutes, then rapidly removed from the furnace, and cooled to room temperature. The specimens were weighed after each cycle; visual evidence of columbium or tantalum oxide constituted coating failure. Tests were run at atmospheric pressure and at pressures of 0.5 and 0.05 mm Hg in dry air (dewpoint less than 0° F). Test temperatures ranged from 2000° F to 2900° F. Atmospheric pressure tests were discontinued at 240 hours if no failures had occurred. Low-pressure tests were discontinued after 20 hours.

Dynamic oxidation tests were conducted on leading-edge segments in an arc jet with a 4-inch-diameter nozzle exhausting to atmospheric pressure. This produced a subsonic airstream with a mass flow of 0.4 pound of air per second. The specimens were exposed to the hot airstream for 6-minute cycles followed by rapid cooling to room temperature for examination. Tests were discontinued when coating failure was observed (visual evidence of columbium or tantalum oxide) or when an accumulated exposure time of 1 hour (10 cycles) was achieved. Temperatures were measured using an optical pyrometer at a wavelength of 0.65 micron with corrections for assumed coating emittances of 0.80 for the silicide and 0.65 for the aluminide.

Tensile tests were performed in a hydraulic testing machine at nominal strain rates of 0.005 per minute to yield and 0.050 per minute to failure. Strains were monitored with optical strain gages which were read while the strain rate was maintained. Tensile elongations were measured over a 1-inch gage length. All tensile tests reported were made at room temperature. Bend tests were made at room temperature on coupon specimens in 3-point bending, using a screw-driven testing machine. The bending span was 1 inch; the ram radius was 1/8 inch; the ram speed was 0.020 inch per minute. Bend angles were calculated from ram deflection recorded during the tests. Specimen curvature was ignored in the calculation. Bend tests were discontinued on evidence of substrate failure or after a 90° bend had been achieved.

Metallurgical procedures and measurements of substrate thicknesses were similar to those of reference 2. The etchant used for the columbium-alloy specimens consisted of 10 parts nitric acid, 10 parts hydrofluoric acid, and 30 parts lactic acid. No etchants were used for the coated tantalum alloy. An electron probe microanalyzer was utilized for embrittlement mechanism studies in the columbium alloy. X-ray emission intensities of various elements were monitored and recorded.

## RESULTS AND DISCUSSION

### Silicide-Coated Columbium-Alloy Sheet

Oxidation. - Results of oxidation tests on the Cr-Ti-Si coated Cb-10Ti-5Zr alloy are shown in figure 1. Arrows indicate that the specimens did not evidence oxidation failure. The graph at the left shows the results of static tests. One-hour cyclic exposure specimens exhibited considerably lower times to failure than continuously exposed specimens and the 6-minute cycles reduced

coating life significantly at temperatures above 2400° F, but adequate oxidation resistance for some thermal protection applications was provided by the coating at temperatures up to at least 2400° F.

The graph at the right in figure 1 shows the results of dynamic oxidation tests on leading-edge segments as compared to results of static tests on coupon specimens in 6-minute cyclic tests (reproduced from the graph at the left). The mass-flow condition further lowered failure times above 2400° F but adequate oxidation lifetimes for some thermal protection applications were again retained to at least 2400° F.

Embrittlement.- The results of room-temperature tensile and bend tests on the silicide-coated columbium alloy are shown in figure 2. In general, these results indicate that significant substrate embrittlement can result from high-temperature exposures at times considerably prior to general coating failure. The curve at the upper left indicates that ultimate tensile strength is not significantly affected by continuous exposures up to 80 hours at 2500° F. However, the corresponding tensile elongation dropped from 14 percent as coated to 4 percent after 5 hours exposure and to 0 after 80 hours exposure as indicated at the lower left of figure 2. The effect of cyclic exposure can be even more severe in terms of embrittlement as determined from bend tests, as indicated in the graph on the right side of figure 2. After continuous exposure for 240 hours at 1 atmosphere and 2000° F, the specimen underwent a ductile 90° bend but under similar conditions in cyclic exposure, a specimen exhibited quite brittle behavior. Again at 1 atmosphere, 2400° F specimens exposed for 155 and 180 hours were progressively more brittle. At reduced pressures after 2400° F cyclic exposures bend test results differed markedly. Specimens subjected to 20-hour exposures at 0.5 mm Hg underwent ductile 90° bends while

specimens which had undergone similar exposures at 0.05 mm Hg were brittle. Metallographic studies in these cases indicated that substrate thickness losses due to solid-state diffusion of silicon were on the order of 0.001 inch at 2500° F for 50 hours. This amount of diffusion would not be expected to produce the substantial embrittlement noted above.

Embrittlement mechanism.- A possible mechanism for this embrittlement will be discussed with the aid of figure 3. In the upper left, the photomicrograph of the specimen which has undergone a ductile 90° bend after a continuous 240-hour exposure at 2000° F. Note the relatively clean grain boundaries in the substrate. At the upper right of figure 3, the specimen which underwent cyclic exposure is shown in a conventional photomicrograph, after cracking along the grain boundaries at a small bend angle. In this figure the grain boundaries show almost continuous precipitate networks. The lower right photograph of figure 3 shows the same area of the cyclic specimen taken by the light of grain boundary fluorescence under the electron beam of the electron probe microanalyzer. This fluorescence suggested that the particles in the grain boundaries might be oxides; the fluorescence was not noted in the continuously exposed specimen. A spectrographic electron probe trace of the embrittled specimen is shown at the lower left of figure 3. It indicates that zirconium in the substrate has concentrated in the grain boundaries. Recent results with the probe modified to detect the low atomic number elements indicate that oxygen has also concentrated at the grain boundaries. No significant grain boundary concentrations of other elements have been noted and no high grain boundary concentrations were noted for any elements in the ductile specimen.

On the basis of this information, it is postulated that oxygen has permeated through microscopic cracks which developed in the coating as a result of the thermal cycling. This oxygen apparently diffused throughout the substrate,

primarily along grain boundaries. The zirconium in the substrate diffused to the grain boundaries and reacted with the oxygen to form an embrittling network of zirconium oxide precipitate particles in the grain boundaries. It is possible that this embrittlement might not be as severe for other columbium alloys as for the Cb-10Ti-5Zr alloy investigated.

#### Aluminide-Coated Tantalum-Alloy Sheet

Oxidation.- Results of oxidation tests on Al-Sn-Mo coated Ta-10W alloy are shown in figure 4. The graph at the left shows the results of static tests on coupons for two cyclic exposure conditions. In the 1-hour cycles at atmospheric pressure lifetimes ranged from about 50 hours at 2000° F to about 5 hours at 2900° F. Reduced pressure tests at both 0.5 and 0.05 mm Hg showed no failures within 20 hours at 2000° F and 2300° F, but indications of some coating evaporation were noted. This effect could severely limit the usefulness of this coating at these reduced pressures and higher temperatures. Equipment limitations have thus far precluded low-pressure testing at higher temperatures in our laboratories. The 6-minute cycles at atmospheric pressure reduced coating life considerably, as compared to the 1-hour cycles.

The graph at the right in figure 4 indicates the effect of dynamic oxidation testing on the life of coated-tantalum-alloy specimens. The static curve is reproduced from the graph at the left for comparison. The dynamic oxidation conditions in the arc-jet tests lowered coating lifetimes obtained under static conditions considerably at temperatures above 2600° F for the aluminide coating containing 5.5 percent molybdenum. A modified aluminide coating containing 7 percent molybdenum has been developed. As shown in figure 4, this coating has exhibited longer lifetimes in the dynamic oxidation tests. Some additional study of this recently developed modification is planned.

A possible explanation for the improvement in dynamic oxidation coating life with an increased molybdenum content in the coating may be arrived at by considering the nature of this coating. As shown in the upper photomicrographs of figure 5, the as-coated specimen on the left contains a layer of one or more aluminides adjacent to the substrate and an outer layer of Al-Sn-Mo. As indicated in the upper right of figure 5, during high-temperature exposure the aluminide layer remains solid but grows by solid-state diffusion of aluminum into the substrate. The Al-Sn-Mo layer is a viscous liquid, with molybdenum aluminide particles acting to increase its viscosity. An outer layer of aluminum oxide forms on the surface of the specimen. It is this outer aluminum oxide layer which is thought to supply the oxidation resistance with the liquid layer underneath supplying aluminum to heal breaks in the outer  $Al_2O_3$  layer. During the dynamic oxidation tests, the liquid layer appeared to flow along the specimens under the shearing action of the airstream, depleting the coating at the stagnation point of the specimen, where failure most often occurs. The new coating with the higher molybdenum content appears to have a more viscous liquid layer, thus resisting this flowing effect and providing longer protection for the substrate.

Embrittlement and diffusion.- In all bend tests of aluminide-coated Ta-10W coupons, the substrate underwent a  $90^\circ$  bend at room temperature without failure. Metallographic investigations indicated no grain boundary embrittlement in specimens in which the coating had not failed. Even for specimens where coating breakdown permitted substrate oxidation, evidence of grain boundary precipitation was limited to regions within approximately  $1/8$  inch of the failure zone.

One factor which could lead to an embrittlement of the coated-tantalum-alloy sheet was noted. This was the loss of substrate thickness due to solid-state diffusion of aluminum into the substrate, widening the brittle aluminide layer at the expense of the substrate. Evidence of this can be noted in the lower photographs of figure 5. The as-coated substrate (lower left) was approximately 0.0075 inch thick. After 20 hours exposure at 2600° F in air, the substrate thickness had decreased 0.002 inch due to the diffusion (lower right, fig. 5). A plot of the substrate thickness loss for specimens of the Al-Sn-Mo coated-tantalum-alloy sheet after various exposure conditions of temperature and time in air at atmospheric pressure is shown in figure 6. It is apparent that there is an increase in substrate thickness loss with increasing temperature from 2000° F to 2300° F for a given exposure time, as would be expected. However, from 2300° F to 2900° F the substrate thickness losses were of approximately the same magnitude for a given exposure time and curves drawn through the points for these temperatures will overlap. Accordingly, all data points for test temperatures from 2300° F to 2900° F have been bracketed in the shaded area of figure 6. A possible explanation for this behavior may be a more rapid increase in the rate of formation of the aluminum oxide layer in the coating compared to that of the aluminide layer with increasing temperatures. This could cause depletion of aluminum in the aluminum-tin-molybdenum layer in the temperature range from 2300° F to 2900° F (ref. 4). Similar results were obtained in reference 7 for aluminide-coated Ta-10W alloy.

#### CONCLUDING REMARKS

Results of investigations on Cr-Ti-Si (silicide) coated Cb-10Ti-5Zr alloy sheet indicated that:

1. At 2400° F the coated sheet exhibited lifetimes longer than 150 hours in static airflow oxidation tests for 1-hour cyclic exposures and longer than 1 hour in dynamic airflow oxidation tests for 6-minute cyclic exposures. This degree of protection may be adequate for some applications in thermal protection systems.

2. During cyclic exposure at atmospheric and reduced pressures, severe substrate embrittlement prior to coating failure was noted at temperatures as low as 2000° F. This embrittlement appears to be caused by permeation of oxygen through microscopic cracks in the coating, diffusion throughout the substrate along grain boundaries, and formation of embrittling networks of zirconium oxide precipitates along grain boundaries.

Test results for Al-Sn-Mo (aluminide) coated Ta-10W alloy sheet indicated that:

1. The coated sheet exhibited lifetimes in excess of 5 hours in static air oxidation tests for 1-hour cyclic exposures at 2900° F and atmospheric pressure. However, indications of coating evaporation were noted in reduced pressure tests at 2300° F.

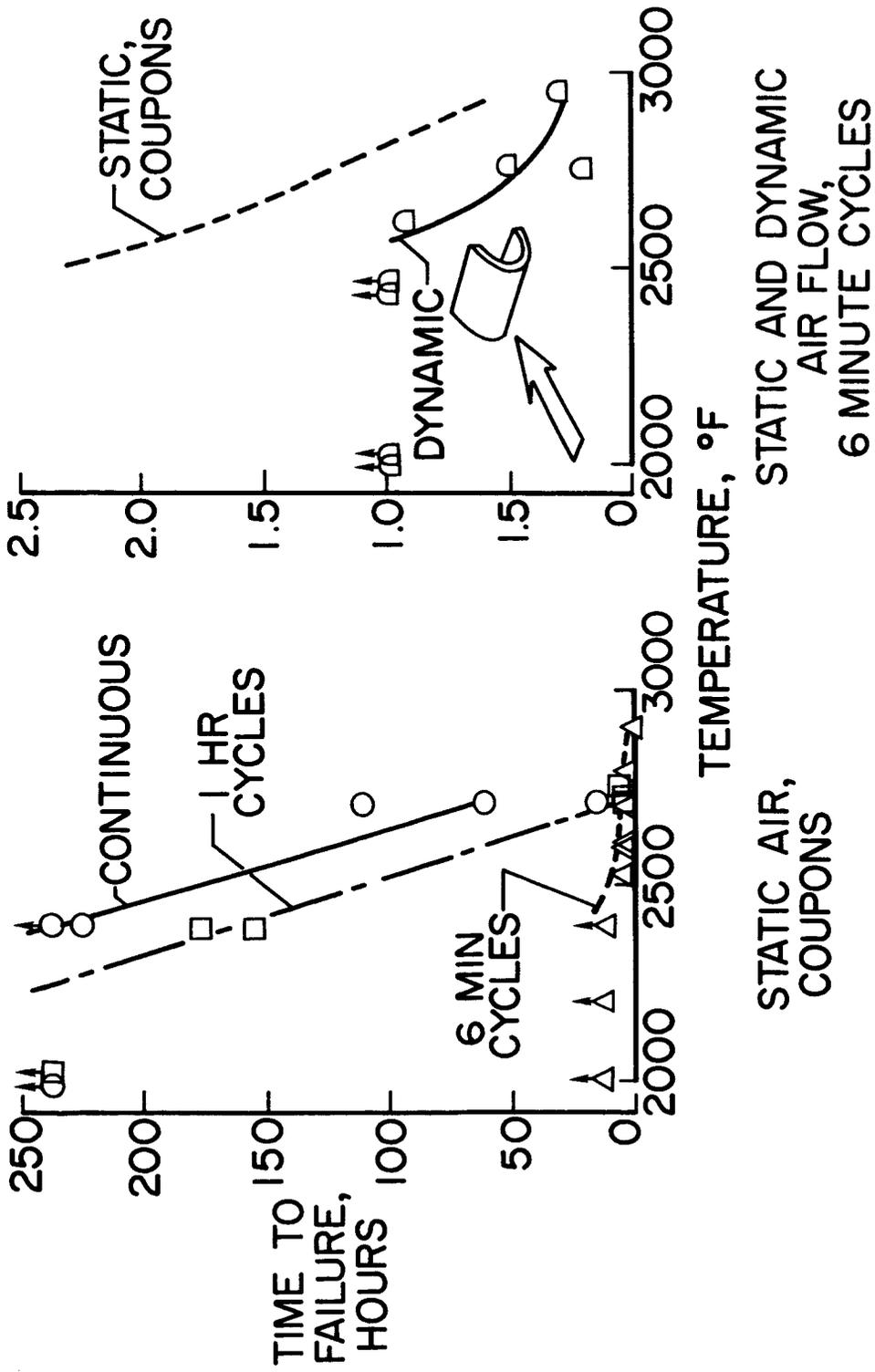
2. Compared to static oxidation test results, dynamic oxidation data at atmospheric pressure indicated considerably lower coating lifetimes for the aluminide coating with 5.5 percent molybdenum. This was apparently due to flowing action in a liquid layer in the coating, produced by the shearing action of the airstream. Preliminary test results on a modified aluminide coating containing 7 percent molybdenum indicated longer lifetimes in the dynamic oxidation tests.

3. No severe embrittlement was noted in bend tests after high-temperature exposures, but loss of substrate thickness due to solid-state diffusion during

high-temperature exposures could limit the applicability of the coated-tantalum-alloy sheet when thin gages are utilized.

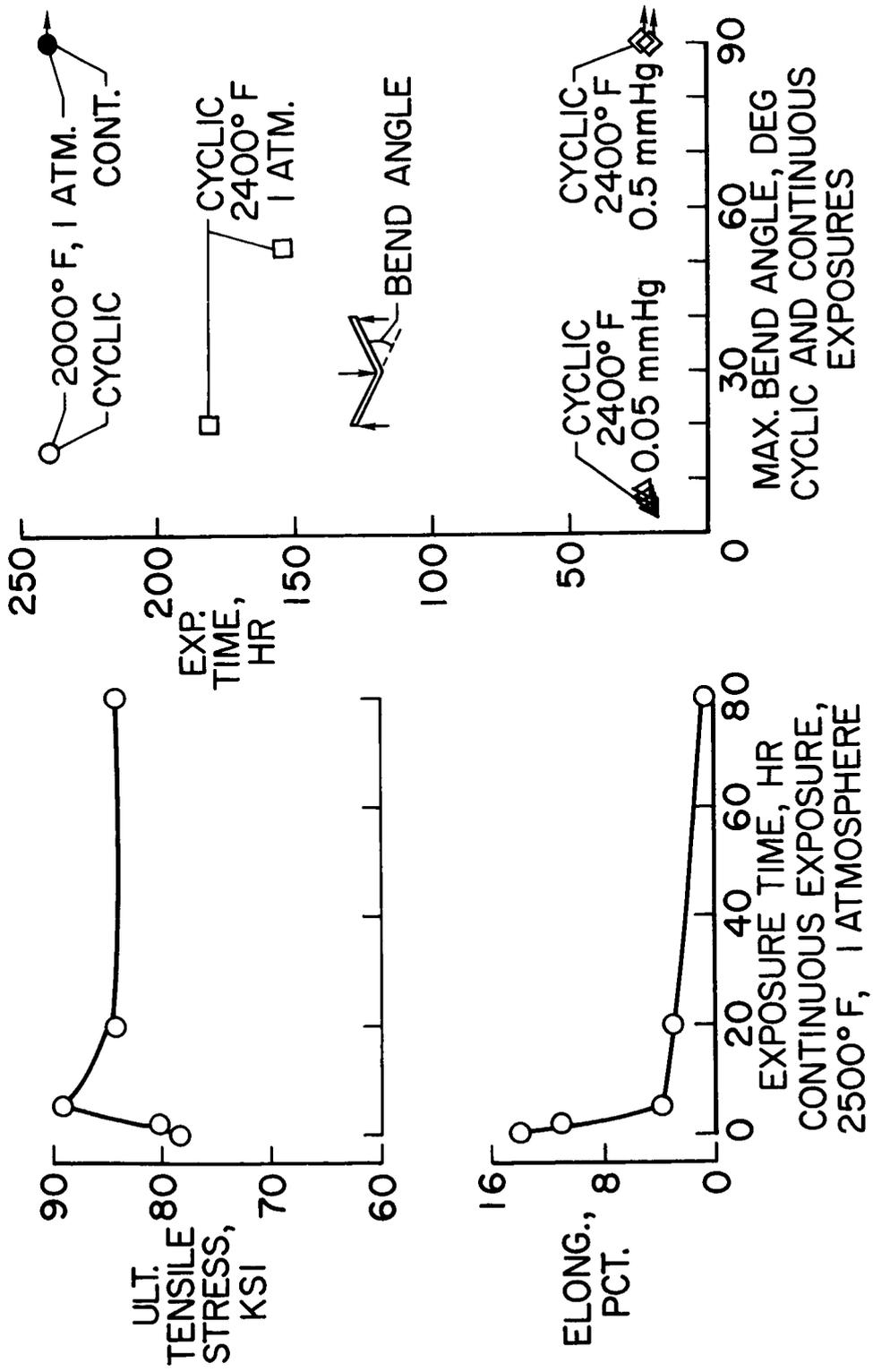
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Figure 1.- Oxidation test results for Cr-Ti-Si (silicide) coated Cb-10Ti-5Zr alloy sheet at atmospheric pressure.

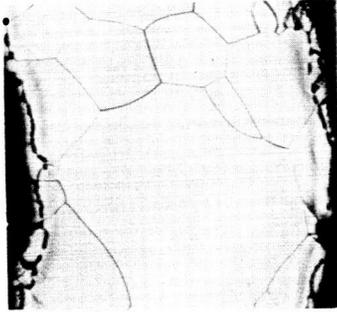


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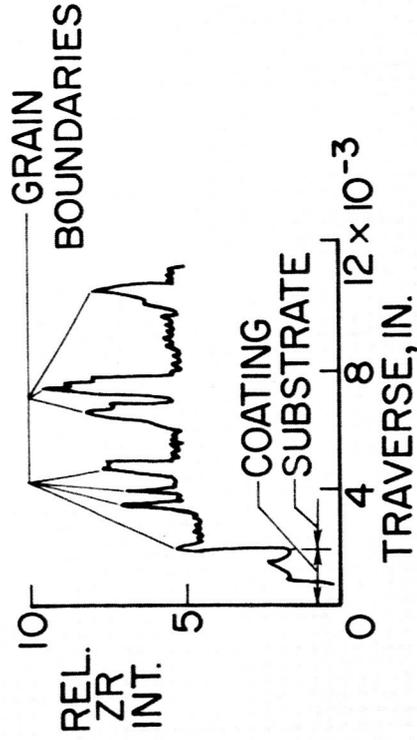
Figure 2.- Room-temperature tensile and bend test results for Cr-Ti-Si (silicide) coated Cb-10Ti-5Zr alloy sheet.



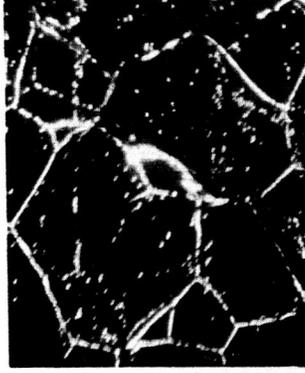
CYCLIC EXPOSURE,  
X100



CONTINUOUS EXPOSURE,  
X100



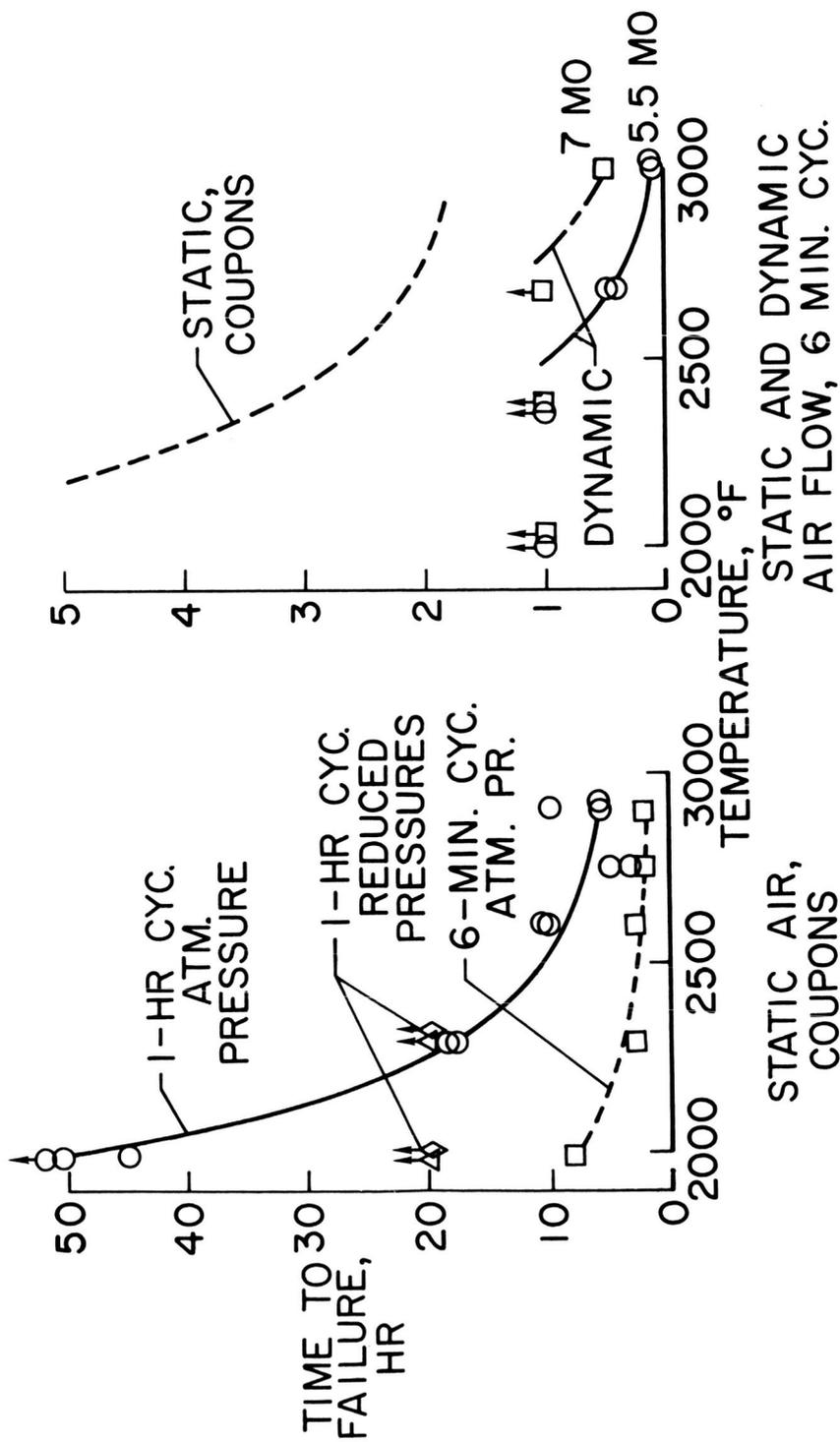
CYCLIC EXPOSURE,  
MICROPROBE TRACE



CYCLIC EXPOSURE,  
FLUORESCENCE UNDER  
ELECTRON BEAM, X150

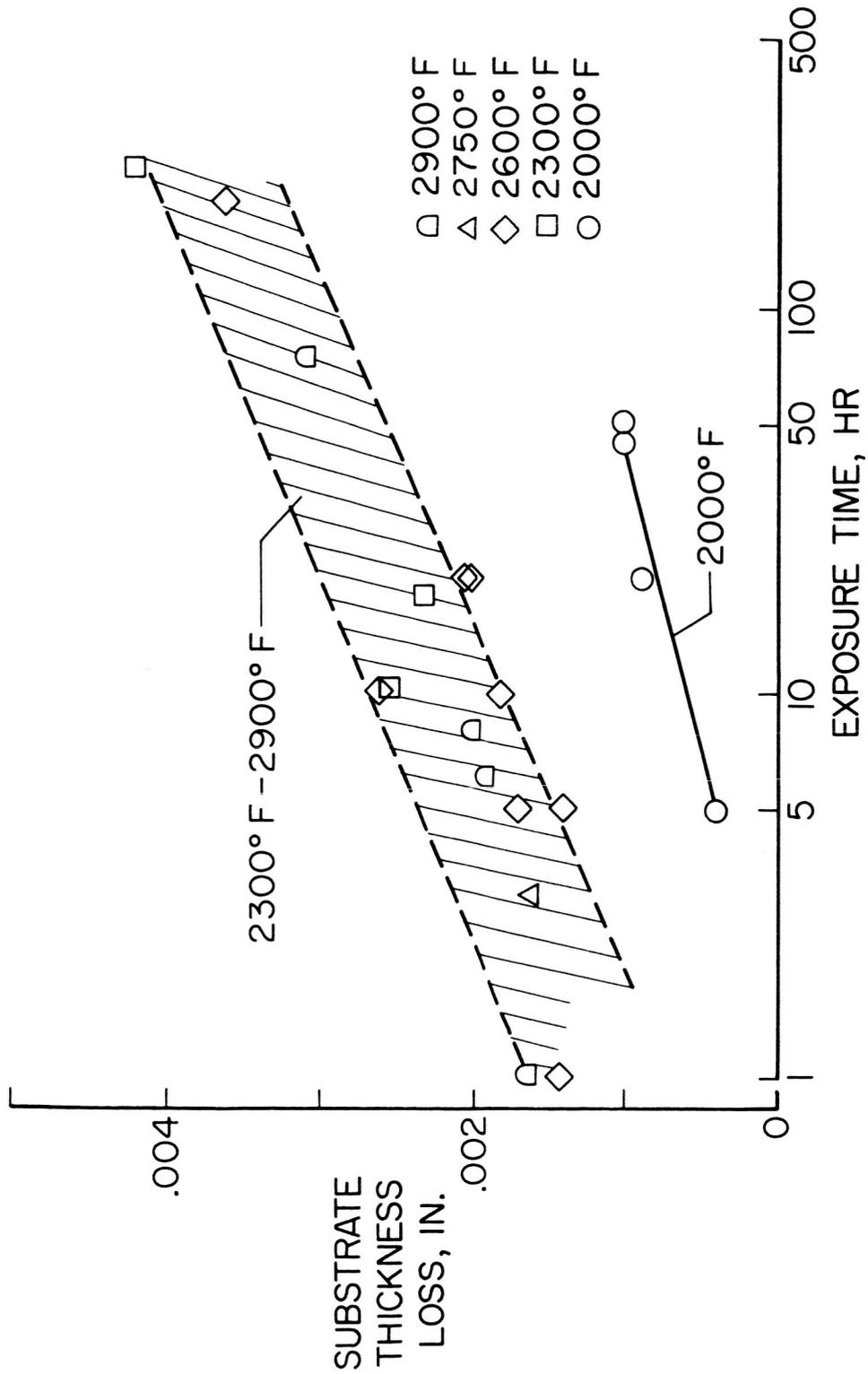
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Figure 3.- Photomicrographs and electron probe trace illustrating embrittlement mechanism for Cr-Ti-Si (silicide) coated Cb-10Ti-5Zr alloy sheet. Specimens exposed for 240 hours at 2000° F, bend tested at room temperature.



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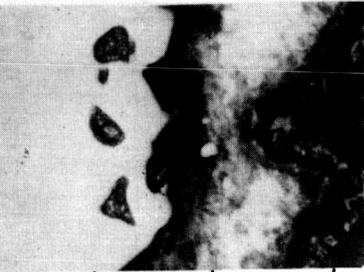
Figure 4.- Oxidation test results for Al-Sn-Mo (aluminide) coated Ta-10W alloy sheet.



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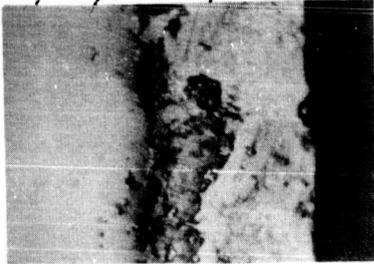
Figure 6.- Variation of substrate thickness loss with exposure time for Al-Sn-Mo (aluminide) coated Ta-10W alloy sheet at several temperatures.

EXPOSED, 1 ATM  
2600° F, 20 HR



X 500

AS COATED



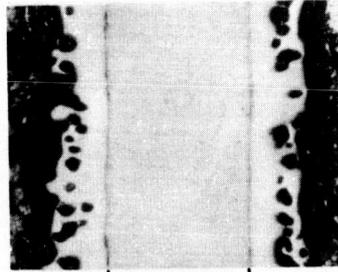
X 500

SUBSTRATE

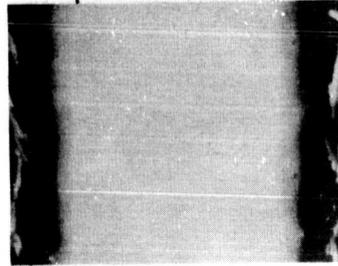
ALUMINIDE

Al - Sn - Mo

$Al_2O_3$



X 200



X 200

SUBSTRATE

Figure 5.- Sections of Al-Sn-Mo (aluminide) coated Ta-10W alloy sheet.